

Verification of Translation

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hereby declare as follows:

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Dated this 18th day of June, 2010



A handwritten signature in black ink, appearing to read "Keiji HABA". The signature is fluid and cursive, with a horizontal line drawn underneath it.

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[Name of Document] **Claims**

[1] A fuel cell power generation system comprising:

 a hydrogen generator including a steam reforming reaction portion configured to generate a hydrogen-rich gas containing carbon monoxide from a fuel containing hydrocarbon and water; a shift converter configured to generate hydrogen and carbon dioxide from the carbon monoxide in the hydrogen-rich gas and the water; and a carbon monoxide removing portion configured to reduce the carbon monoxide in the hydrogen-rich gas which has not been removed in said shift converter;

 a fuel cell configured to generate power using the hydrogen-rich gas supplied from said hydrogen generator and an oxidizing gas;

 an air supply portion configured to supply air to at least one of (1) a position upstream of said steam reforming reaction portion in a flow of the fuel, (2) a position between the shift converter and the carbon monoxide removing portion, and (3) a position between said carbon monoxide removing portion and said fuel cell in the flow of the fuel; and

 an impurity removing means configured to remove an impurity from the air.

[2] The fuel cell power generation system according to claim 1, wherein said impurity removing means has an adsorbing agent or an absorbing agent of hydrogen sulfide.

[3] The fuel cell power generation system according to claim 1 or 2, wherein said impurity removing means has an adsorbing agent or an absorbing agent of sulfur oxide.

[4] The fuel cell power generation system according to claims 1 to 3, wherein said impurity removing means has a catalytic combustor.

[5] The fuel cell power generation system according to claim 3, wherein said impurity removing means has a catalytic combustor located upstream of the adsorbing agent or the absorbing agent of the sulfur oxide in a flow of the air.

[6] The fuel cell power generation system according to claim 4 or 5, wherein said catalytic combustor is positioned to exchange heat with said hydrogen generator or with an exhaust gas resulting from combustion which is used to heat said hydrogen generator.

[7] The fuel cell power generation system according to claim 3 or 5, wherein the adsorbing agent or the absorbing agent of the sulfur oxide is positioned to exchange heat with said hydrogen generator or with an exhaust gas resulting from combustion which is used to heat said hydrogen generator.

[8] The fuel cell power generation system according to claim 5, wherein said catalytic combustor functions as the adsorbing agent or the absorbing agent of the sulfur oxide and has a catalyst containing noble metal and alkaline earth metal, said catalytic combustor being positioned to exchange heat with said hydrogen generator or with an exhaust gas resulting from combustion which is used to heat said hydrogen generator.

[Name of Document] specification

[Title of the Invention] fuel cell power generation system

[Technical Field]

[0001] The present invention relates to a fuel cell power generation system. More particularly, the present invention relates to a fuel cell power generation system that includes a hydrogen generator configured to cause a fuel containing hydrocarbon and water to flow through a catalyst to generate a hydrogen-rich gas containing carbon monoxide and that is configured to remove an impurity from air flowing through the hydrogen generator or an anode.

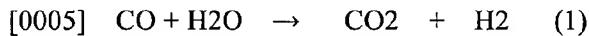
Background Art

[0002] Polymer electrolyte fuel cells (Hereinafter referred to as PEFCs) generate electricity using oxygen and hydrogen. The impurities in air supplied to a cathode of the PEFC causes a voltage drop. Therefore, a catalytic combustor for removing impurities such as organic solvent has been proposed (for example, patent document 1)

[0003] An industrial manufacturing method of hydrogen is, for example, electrolysis of water. As other methods, a steam reforming method of hydrocarbon gas, a partial oxidation method of the hydrocarbon gas, and an autothermal method including a combination of these two methods. In these reforming methods, methane, ethane, propane, butane, city gas, LP gas, or other hydrocarbon gas (including a mixture gas of hydrocarbon of two kinds or more) is reformed to generate a hydrogen-rich gas. In any case, a reformer is used. The concentration of the carbon oxide (hereinafter referred to as CO) contained in a fuel hydrogen which is supplied to the PEFC is required to be limited to approximately 50ppm (concentration based on capacity, the same occurs hereinafter). If the concentration is above approximately 50ppm, performance of the fuel cell significantly degrades. It is therefore necessary to remove the CO as much as

possible before the fuel hydrogen is introduced to the PEFC.

[0004] The steam-reformed gas generated in the steam reforming typically contains 8 to 15% (concentration based on capacity) CO as a side-reaction product, which may vary depending on the performance of the steam reforming reaction portion, as well as unreacted methane, unreacted steam and carbon dioxide gas. In order to remove this side-reaction product CO, the reformed gas is led to a shift converter. In the shift converter, the CO is converted into carbon dioxide and hydrogen through a shift reaction (1). The reformed gas generated through the shift converter, contains a minute amount of CO. For this reason, in a CO selective oxidation portion, an oxidizing gas such as air is added to cause CO selective oxidation (2) to occur to reduce the concentration of the CO to 50ppm or less, preferably 10ppm or less. The resulting hydrogen-rich gas is supplied to an anode of the PEFC. Against an increase in CO concentration, for example, due to fluctuation of a load, air is commonly supplied to the anode to conduct air-breathing in order to inhibit CO poisoning in an anode electrocatalyst.



It is desirable to stop components in a fuel cell for household use to increase efficiency when power consumption is less. In this case, it is necessary to purge fuel or hydrogen, from the interior of the fuel cell, using an incombustible gas for the purpose of safety. However, since it is difficult to install a N₂ cylinder at the fuel cell for household use, there has been disclosed a method in which the remaining gas is purged from the hydrogen generator and an anode passage using steam, and then the steam is purged therefrom using air in a temperature range in which steam condensation does not occur.

[Patent document 1] Japanese Laid-Open Patent Application Publication No. 2000-277139

[Disclosure of the Invention]**[Problems to be Solved by the Invention]**

[0006] As air supplied to the catalyst and electrocatalyst in the interior of the hydrogen generator, in addition to the cathode, there are anode air breathing air, selective oxidation air, and purge air in at the stop of a system.

[0007] The supply amount of the air used in the above is less than the supply amount of the air supplied to the cathode of the fuel cell. In the case of the fuel cell of 1kW, the supply amount of the air to the cathode is 65Nl/min (hereinbelow expressed in this way in terms of 0°C and 1atm), while the supply amount of the air for anode air-breathing air, the selective oxidation air and the purge air at the stop of the system are 0.3Nl/min, 0.5Nl/min, 100Nl/one time, respectively.

[0008] Exemplary impurities contained in the air are inorganic gases such as sulfur oxide, hydrogen sulfide, nitrogen oxide, and ammonia, and organic gases such as amine, fatty acid, aromatic compounds, and aldehyde. The concentration of these gases is as low as several tens ppm to several ppb.

[0009] The reaction occurring in the anode during the air-breathing and the reaction occurring in the CO selective oxidation are oxidation reactions, and therefore are less affected in the case of easily combustible substances such as acetic aldehyde. Also, the catalyst operating temperature of the steam reforming reaction , the shift catalyst, and the selective oxidation catalyst are about 700 degrees C, about 300 degrees C, and about 150 degrees C, and are higher than the cathode catalyst operating temperature (70 – 80 degrees C). Therefore, poisoning substances are easily removed.

[0010] However, in a case where the impurities such as sulfide oxide or hydrogen sulfide, i.e., so-called permanent poisoning substances, active site of the catalyst will be covered with them and thereby catalyst characteristic will be finally degraded, if the

catalyst is exposed to the poisoning substances for a long time period of, for example, several tens thousands hours.

[0011] It is believed that the permanent poisoning substance poisons a noble metal catalyst noticeably, if it covers an exposed surface of the noble metal in a ratio of approximately 1/several tens to 1/2. In a fuel cell of 1kW, Pt and Ru used as an anode catalyst of the fuel cell are respectively about 0.02mol. If air containing 0.5ppm hydrogen sulfide is supplied to the anode at 0.3Nl/min for air-breathing, poisoning substances are accumulated to the amount that may negatively affect the catalyst in several thousands to several tens thousands hours.

[0012] In the case of selective oxidation, assuming that the fuel cell of 1kW treats a gas containing CO of several thousands ppm, it is necessary to supply air at 0.5Nl/min. In the case of using 200cc of honeycomb of Ru6g/l, poisoning substances are accumulated to the amount that may negatively affect the catalyst in several hundreds to several thousands hours, if air containing of hydrogen sulfide of 0.5ppm is supplied.

[0013] In a case where hydrogen generator purge air is supplied through an inlet of the steam reforming reaction portion, Ru catalyst which is a steam reforming catalyst is degraded noticeably. Specifically, when 300g of 2wt% Ru/alumina catalyst is used as the reforming catalyst, the amount of Ru is 0.06mol. It is assumed that if the air containing 0.5ppm hydrogen sulfide is flowed at 100Nl per purge operation, the poisoning substance is accumulated to the amount that may negatively affect the catalyst after the purge operations several hundreds times or several thousands times. The fuel cell system that performs start-up and stop operations every day performs the start-up and stop operations 3650 times for ten years. So, in a long-time use, this effect is negligible.

[0014] Thus far, hydrogen sulfide has been described. The concentration of the

hydrogen sulfide in the air may be 0.05 to 10ppm only in volcano areas or hot spring areas. Since the sulfur oxide is easily converted into hydrogen sulfide under reduction atmosphere in which hydrogen exists on the noble metal catalyst, it may sometimes affect degradation of catalyst as in the hydrogen sulfide, depending on the type of the catalyst and gas atmosphere. Since Japanese environmental criteria of sulfur oxide concentration is 0.04ppm, the sulfur oxide may affect the catalyst in the long term in the fuel cell installed near roads with a lot of traffic volumes.

[0015] For example, toluene which is an organic compound contained in a paint or the like is incombustible and is not substantially oxidized and decomposed at 200°C or lower even if noble metal catalyst is used. So, it remains on the catalyst and acts as a poisoning substance under temperature conditions in which the anode electrocatalyst or selective oxidation catalyst operates. According to Foul Smell Control Law in Japan, regulation criterion of toluene is 10ppm in a primary area. In places where smell of paint is always filling, influence of toluene is significant. Likewise, in environments where incombustible organic substances (including fatty acid) are always present, the organic substances may cause catalyst poisoning. The influence of the nitrogen oxide is reversible. The nitrogen oxide is easily removed and therefore does not stay on the catalyst. Thus, the influence of nitrogen oxide is less.

[0016] The present invention has been made in view of the above mentioned problems associated with the art. An object of the present invention is to provide a fuel cell system that is capable of maintaining a stable operation for a long-time period by removing impurities from air which is supplied thereto.

[Means for Solving the Problem]

[0017] To achieve the above objective, a fuel cell power generation system of a first invention comprises: a hydrogen generator including a steam reforming reaction portion

configured to generate a hydrogen-rich gas containing carbon monoxide from a fuel containing hydrocarbon and water; a shift converter configured to generate hydrogen and carbon dioxide from the carbon monoxide in the hydrogen-rich gas and the water; and a carbon monoxide removing portion configured to reduce the carbon monoxide in the hydrogen-rich gas which has not been removed in said shift converter;

a fuel cell configured to generate power using the hydrogen-rich gas supplied from said hydrogen generator and an oxidizing gas;

an air supply portion configured to supply air to at least one of (1) a position upstream of said steam reforming reaction portion in a flow of the fuel, (2) a position between the shift converter and the carbon monoxide removing portion, and (3) a position between said carbon monoxide removing portion and said fuel cell in the flow of the fuel; and

an impurity removing means configured to remove an impurity from the air.

[0018] In a second invention, said impurity removing means has an adsorbing agent or an absorbing agent of hydrogen sulfide.

[0019] In a third invention, said impurity removing means has an adsorbing agent or an absorbing agent of sulfur oxide.

[0020] In a fourth invention, said impurity removing means has a catalytic combustor.

[0021] In a fifth invention, said impurity removing means has a catalytic combustor located upstream of the adsorbing agent or the absorbing agent of the sulfur oxide in a flow of the air.

[0022] In a sixth invention, said catalytic combustor is positioned to exchange heat with said hydrogen generator or with an exhaust gas resulting from combustion which is used to heat said hydrogen generator.

[0023] In a seventh invention, adsorbing agent or the absorbing agent of the sulfur

oxide is positioned to exchange heat with said hydrogen generator or with an exhaust gas resulting from combustion which is used to heat said hydrogen generator.

[0024] In an eighth invention, said catalytic combustor functions as the adsorbing agent or the absorbing agent of the sulfur oxide and has a catalyst containing noble metal and alkaline earth metal, said catalytic combustor being positioned to exchange heat with said hydrogen generator or with an exhaust gas resulting from combustion which is used to heat said hydrogen generator.

[Effects of the Invention]

[0025] In accordance with the present invention, it is possible provide a fuel cell system capable of maintaining a stable operation for a long period.

Best Mode for Carrying Out the Invention

[0026] Hereinafter, embodiments of the present invention will be described with reference to the drawings.

[0027] (Embodiment 1)

Fig. 1 is a view schematically showing a construction of a fuel cell power generation system according to an embodiment 1 of the present invention. As shown in Fig. 1, the fuel cell system of the embodiment 1 comprises a hydrogen generator 20 configured to generate a hydrogen-rich gas. The hydrogen generator 20 includes a steam reforming reaction portion 1 which is filled with Ru/alumina catalyst and is configured to generate a hydrogen-rich gas containing carbon monoxide from fuel gas containing hydrocarbon and water. The hydrogen generator 20 further includes a shift converter 2 which is positioned downstream of the steam reforming reaction portion 1 in a flow of the gas and is filled with Pt/CeZrO_x catalyst which is an oxidation resistant shift reaction catalyst. The shift converter 2 reduces side-reaction product CO produced in the steam reforming reaction portion 1. The hydrogen generator 20 further includes a

CO selective oxidation portion (carbon monoxide removing portion) 3 which is positioned downstream of the shift converter 2 and is filled with Ru/alumina catalyst which is the selective oxidation catalyst. The CO selective oxidation portion 3 further reduces the CO which has not been completed in the shift converter 2.

[0028] A polymer electrolyte fuel cell 4 which is an example of the fuel cell of the present invention is installed downstream of the CO selective oxidation portion 3 and is configured to generate power using the hydrogen-rich gas containing reduced CO as an anode gas. By way of example, an anode catalyst of the fuel cell is Pt – Ru/C catalyst. The fuel cell system of the embodiment 1 is equipped with a cathode air supply portion 10 configured to supply, to a cathode side of the polymer electrolyte fuel cell 4, air from which impurities have been removed.

[0029] A purge air supply portion 6 is positioned upstream of the steam reforming reaction portion to supply, to the steam reforming reaction portion 1, air for purging a remaining gas from the fuel cell system in a stopped state of the fuel cell system. In addition, a CO selective oxidation air supply portion 8 is provided between the shift converter 2 and the selective oxidation portion 3 to supply air to the CO selective reaction portion 3. Further, an anode air-breathing air supply portion 9 is provided between the CO selective oxidation portion 3 and the polymer electrolyte fuel cell 4.

[0030] The fuel cell system of the embodiment 1 further comprises a hydrogen sulfide absorbing portion 5 configured to remove hydrogen sulfide from the air supplied to each of the purge air supply portion 6, the CO selective oxidation air supply portion 8, and the anode air-breathing air supply portion 9. A heat exchanger 11 is positioned downstream of the hydrogen sulfide absorbing portion 5 in a flow of the air. The heat exchanger 11 is disposed in contact with the CO selective oxidation portion 3 to exchange heat with the CO selective oxidation portion 3. A catalytic combustor 12 having a Pt/alumina catalyst

is positioned downstream of the heat exchanger 11. The catalytic combustor 12 is disposed in contact with the shift converter 2 to exchange heat with the shift converter 2. A sulfur oxide absorbing portion 13 having calcium oxide is positioned downstream of the catalytic combustor 12. The sulfur oxide absorbing portion 13 is disposed to exchange heat with the shift converter 2. The air is supplied from the sulfur oxide absorbing portion 13, to the purge air supply portion 6, the CO selective oxidation air supply portion 8, and the anode air-breathing air supply portion 9. A valve 7 is provided between the purge air supply portion 6 and the sulfur oxide absorbing portion 13.

[0031] An operation of the fuel cell system of the embodiment 1 configured as described above will be described hereinhereinafter.

[0032] Referring to Fig. 1, a fuel that has flowed through an adsorbing agent that adsorbs and removes a sulfur component from the fuel is mixed with water, heated, and is introduced into the steam reforming reaction portion 1. The temperature of the steam reforming catalyst varies depending on the type of the fuel. When the fuel is the city gas, the city gas which has just exited from the steam reforming catalyst is kept at approximately 650°C. The hydrogen-rich gas generated in the steam reforming reaction portion 1 flows through the shift converter 2, and the CO selective oxidation portion 3. Thereby, the side-reaction product CO generated in the steam reforming reaction portion 1 is reduced. The resulting hydrogen-rich gas is supplied to the polymer electrolyte fuel cell 4 as the anode gas.

[0033] The air flows through the hydrogen sulfide absorbing portion 5 and is heated in the heat exchanger 11 in contact with the CO selective oxidation portion 3.

[0034] Then, the air flows through the catalytic combustor 12 kept at 250°C during a normal operation, and thereafter flows through the sulfur oxide absorbing portion 13 kept

at 300°C. The catalytic combustor 12 and the sulfur oxide absorbing portion 13 are in contact with the shift converter 2 and are heated. It shall be understood that the hydrogen sulfide is oxidized into the sulfur oxide on the Pt/alumina catalyst, and is absorbed into the sulfur oxide absorbing portion 13 if the hydrogen sulfide absorbing portion 5 is omitted. Nonetheless, since a part of the hydrogen sulfide remains on the Pt/alumina catalyst, it is therefore desirable to remove the hydrogen sulfide in advance in the hydrogen sulfide absorbing portion 5.

[0035] After flowing through the sulfur oxide absorbing portion 13, the air is sent, through the CO selective oxidation air supply portion 8 and the anode air-breathing air supply portion 9, to the CO selective oxidation portion 3 and the anode of the polymer electrolyte fuel cell 4 at, for example, 0.5Nl/min and 0.3Nl/min, respectively.

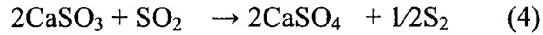
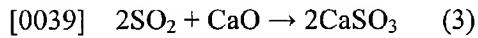
Alternatively, the air that gas flowed through the sulfur oxide absorbing portion 13 may be supplied to the cathode air supply portion 10 and used as the cathode air.

[0036] A combustible gas such as hydrogen or the city gas remaining within the system in a stopped state of the fuel cell is hazardous and therefore must be purged from the system using air. In the embodiment 1, after the device is cooled to a temperature at which the steam reforming catalyst Ru is not oxidized, the valve 7 is opened.

[0037] After flowing through the sulfur oxide absorbing portion 13, the air is supplied to the steam reforming reaction portion 1, through the purge air supply portion 6, to sequentially replace the combustible gas remaining in the shift converter 2, the CO selective oxidation portion 3, and the polymer electrolyte fuel cell 4 at 10Nl/min for 10 minutes, for example.

[0038] It is desirable to use alkaline earth metal oxides, oxides of transition metals such as Mn, Co, Fe, Cu, or Zr, oxides of rare earth metal such as Ce, as the adsorbing agent or the absorbing agent of the sulfur oxide in the sulfur oxide absorbing portion 13. Some

of the absorbing agent is desirably heated for use. In the case of CaO, the sulfur oxide is absorbed into CaO at 300 to 600°C according to formulae (3) and (4) represented below.



Alternatively, alkaline component impregnated charcoal and zeolite may be used as sulfur oxide absorbing agents.

[0040] Exemplary hydrogen sulfide adsorbing agents of the hydrogen sulfide absorbing portion 5 are zeolite such as MS4A and the alkaline component impregnated charcoal.

[0041] Exemplary catalyst for causing the organic compound to combust in the catalytic combustor 12 is Pt/alumina. Pt – Rh based catalyst having resistance to sulfur poisoning is desirably used in the catalytic combustor 12. Since the hydrogen sulfide is converted into the sulfur oxide using the combustion catalyst having resistance to sulfur poisoning and high oxidation activity, the hydrogen sulfide absorbing portion 5 may be omitted. While organic compound is desirably catalytically combusted for maintenance-free, it may be adsorbed and removed by using active carbon filter or the like.

[0042] (Embodiment 2)

Fig. 2 is a view schematically showing a construction of a fuel cell power generation system according to an embodiment 2 of the present invention. As shown in Fig. 2, the fuel cell system of the embodiment 2 is identical to that of the embodiment 1 except that the catalytic combustor 14 has sulfur oxide absorbing capability. In Fig. 2, the same reference numerals as those in Fig. 1 denote the same or corresponding parts, which will not be described in detail. Hereinbelow, difference will be described.

[0043] The catalytic combustor 14 in the fuel cell system of the embodiment 2 has a

pellet-shaped catalyst carrying barium oxide and platinum on alumina. The catalytic combustor 14 corresponds to the catalytic combustor 12 and the sulfur oxide absorbing portion 13 of the embodiment 1. Sulfur dioxide or hydrogen sulfide is oxidized into sulfur trioxide on heated noble metal and is absorbed into barium oxide present in the vicinity of the noble metal. The barium oxide is exemplary and other alkaline earth metal oxides such as calcium oxide may be used.

[0044] The noble metal catalyst allows organic substances such as toluene and sulfur compounds to be combusted at relatively low temperatures. In the manner described above, the organic compound, the sulfur oxide, and the hydrogen sulfide are effectively removed.

[0045] The carbon monoxide removing portion of the present invention, which corresponds to the CO selective oxidation portion 3 in the embodiments 1 and 2, may remove carbon monoxide by methanation reaction rather than the CO selective oxidation, or otherwise reduce the CO by using a combination of the methanation reaction and the CO selective oxidation so long as the carbon monoxide is reduced as much as possible in the hydrogen-rich gas supplied from the shift converter 2. When only the methanation reaction is conducted in the carbon monoxide removing portion, the CO selective oxidation air supply portion may be omitted.

[0046] The impurity removing portion of the present invention corresponds to the hydrogen sulfide absorbing portion 5, the heat exchanger 11, the catalytic combustor 12, and the sulfur oxide absorbing portion 13 in the embodiment 1, and to the hydrogen sulfide absorbing portion 5, the heat exchanger 11, and the catalytic combustor 14 in the embodiment 2. Alternatively, as described above, the hydrogen sulfide absorbing portion 5 may be omitted. Nonetheless, since a part of the hydrogen sulfide remains on the Pt/alumina of the catalytic combustor 12, it is desirably removed in advance in the

hydrogen sulfide absorbing portion 5.

[0047] The air supply portion positioned upstream of the steam reforming reaction portion of the present invention corresponds to the purge air supply portion 6 of the embodiments 1 and 2. The air supply portion provided between the shift reaction portion and the carbon monoxide removing portion of the present invention corresponds to the CO selective oxidation air supply portion 8 of embodiments 1 and 2. Also, the air supply portion of the present invention positioned between the carbon monoxide removing portion and the fuel cell corresponds to the anode air-breathing air supply portion 9 of the embodiments 1 and 2. While in the embodiment 1, the impurity is removed from the air supplied from the purge air supply portion 6, the air supplied from the CO selective oxidation air supply portion 8 and from the air supplied to the anode air-breathing air supply portion 9, it may alternatively be removed from the air supplied from one of them. Nonetheless, in order to carry out stable operation for a long time period, the impurity may be removed from all of the air supplied.

[0048] The catalytic combustor 12 and the sulfur oxide absorbing portion 13 of the embodiment 1 are disposed in contact with the shift converter 2 and is configured to exchange heat with the shift converter 2. Alternatively, the catalytic combustor 12 and the sulfur oxide absorbing portion 13 may be disposed to exchange heat with an exhaust gas resulting from combustion which is used to heat the shift converter 2 without contacting the shift converter 2, or otherwise may be disposed in contact with the CO selective oxidation portion 3 or the like instead of the shift converter 2, so long as the catalytic combustor is heated up to a temperature suitable for catalytic combustion and the sulfur oxide absorbing portion 13 is heated up to a temperature suitable for absorption or adsorption of the sulfur oxide. The same applies to the catalytic combustor 14 of the embodiment 2.

Examples

[0049] Hereinafter, examples of the fuel cell power generation system and the operation method thereof will be described.

[0050] **(Example 1)**

In an example 1, a membrane electrode assembly (hereinafter referred to as MEA) was produced. Gas and air were caused to flow through the MEA to conduct test of influence of the impurities in the air.

[0051] First, a manufacturing method of the MEA will be described.

[0052] Water and perfluorosulfonic acid ionomer ethanol solution (Flemion: 9wt% perfluorosulfonic acid ionomer produced by ASAHI Glass Co. Ltd) were added to Pt/C catalyst, and catalyst ink was adjusted so that weight ratio of Flemion to carbon black was 1:1. The catalyst ink was applied to a carbon paper by a doctor blade method such that the amount of Pt was 0.3mg/cm^2 and was dried at 60°C , thereby producing a cathode gas diffusion electrode layer.

[0053] An anode gas diffusion electrode layer was produced from 30wt%Pt – 24wt%Ru/C such that the amount of Pt was 0.3mg/cm^2 in the same manner.

[0054] A Nafion 112 membrane (registered mark, produced by Dupont) was sandwiched between the two gas diffusion electrode layers produced as described above and was joined by hot pressing at 130°C , thereby manufacturing the membrane electrode assembly (MEA).

[0055] The MEA was caused to operate using air and hydrogen under the condition in which oxygen utilization ratio was 40%, hydrogen utilization ratio was 70%, cell temperature was 75°C , cathode dew point was 65°C , anode dew point was 70°C and output current was 0.2A/cm^2 . In this case, a gas mixture containing simulation gas of 50ppm CO – 20% CO_2H_2 and 0.0013Nl/min air containing 20ppm hydrogen sulfide was

flowed through the anode. An output voltage of the MEA was 0.715V in an initial stage at start of power generation, but decreased to 0.642V after an elapse of 1000 hours.

[0056] An experiment was conducted in such a manner that air containing 20ppm hydrogen sulfide was flowed through a hydrogen sulfide absorbing agent filled with pellets of zeolite (MS4A), and then through the MEA. As a result, the voltage was 0.707V after an elapse of 1000 hours, and thus voltage drop was suppressed.

[0057] Thus, it has been found that the voltage drop occurred in the MEA when the hydrogen sulfide was present as the impurity in the anode air-breathing air, and was suppressed by the impurity removing agent that removes the hydrogen sulfide.

[0058] **(Example 2)**

A CO selective oxidation catalyst comprised of a honeycomb carrying 1.5g/l Ru and having a diameter of 2cm and a thickness of 1cm was used. 0.5%CO – 20%CO₂/H₂ tank was used. A gas having a dew point of 70°C was created and model test was conducted. Air was supplied so that O₂/CO was 1.5. 20ppm of SO₂ was mixed into this air. GHSV was set to 9300h⁻¹. The test gas was flowed through the CO selective oxidation catalyst at a catalyst temperature of 150°C for 10h. The CO concentration on an exit side of the CO selective oxidation catalyst was 112ppm just after the test gas started to be flowed, but increased up to 322ppm after an elapse of 10 hours.

[0059] In contrast, likewise, an experiment is conducted in such a way that air containing SO₂ of 20ppm was flowed through a CO selective oxidation catalyst through an sulfur oxide absorbing agent filled with impregnated active carbon. As a result, the CO concentration after 10 hours was 121ppm and there was a change in the CO concentration.

[0060] As should be appreciated, it is found out that if air introduced into the CO selective oxidation catalyst contains impurities, a characteristic degrades. The impurity

removing agent was able to suppress this.

[0061] **(Example 3)**

Methane humidified in S/C (steam/carbon) ratio of 3:1 was flowed through 1.3cc of 2wt%Ru/alumina catalyst pellets under the condition in which GHSV was 3200h^{-1} and the temperature was 640°C to be subjected to steam reforming. As a result, the conversion was 86%. Thereafter, the catalyst pellets were cooled to a room temperature, and then air containing 20ppm hydrogen sulfide was flowed through the catalyst pellets at 0.25NLmin for 20h. Thereafter, the steam reforming reaction was conducted under the same conditions, and the conversion was measured. As a result, the conversion decreased to 70%.

[0062] In a similar test, air containing 20ppm hydrogen sulfide was flowed through a hydrogen sulfide absorbing agent filled with MS4A pellets. After flowing the air through the catalyst for 20h, the characteristic of the steam reforming catalyst was measured, and the conversion was 85%.

[0063] As described above, it was found out that the steam reforming catalyst degraded if the air for purging contains impurities.

[0064] **(Example 4)**

Fig. 3 is a view schematically showing a construction of a fuel cell power generation system according to an example 4. While the fuel cell system of the example 4 is identical in basic construction to the fuel system of the embodiment 1, the hydrogen sulfide absorbing portion 5 is omitted in the example 4, and the example 4 shows the construction in more detail. Therefore, the configuration which is not illustrated in the embodiment 1 will be described.

[0065] As shown in Fig. 3, the fuel cell system of the example 4 comprises a fuel supply portion 15 configured to supply the city gas 13A. A zeolite based adsorption

and desulfurization portion 16 is disposed downstream of the fuel supply portion 15. A water supply portion 17 is connected to a position of the gas passage which is downstream of the zeolite based adsorption and desulfurization portion 16. A water evaporator 18 is disposed downstream of the water supply portion 17. The steam reforming reaction portion 1 is cylindrical. The water evaporator 18 is disposed on an outer periphery of the cylindrical steam reforming reaction portion 1 to enable waste heat in the steam reforming reaction to be utilized. A steam reforming reaction portion heater 19 including an off gas burner is installed at the center of the steam reforming reaction portion 1 and is configured to heat the steam reforming reaction portion 1. The steam reforming reaction portion heater 19 heats the steam reforming reaction portion 1 by combusting an anode off gas exhausted from the fuel cell 4. Ru catalyst is disposed around the off gas burner. The city gas containing steam was supplied to the Ru catalyst from above to below.

[0066] The steam reforming reaction portion 1 was filled with 0.3L Ru catalyst. The shift converter 2 was filled with 2L Pt/CeZrO_x catalyst. The CO selective oxidation portion 3 was filled with 0.2L Ru catalyst. The CO selective oxidation catalyst was comprised of a honeycomb structure catalyst body and other catalysts was comprised of a pellet-shaped catalyst body.

[0067] Using the fuel cell system of the example 4 constructed above, an experiment was conducted as described below.

[0068] The city gas 13A was supplied from the fuel supply portion 15 at 4Nl/min. The water adjusted to have S/C of 3 was supplied from the water supply portion 17 to the steam reforming reaction portion 1. The combustion amount in the steam reforming reaction portion heater 19 was adjusted so that the temperature of the Ru catalyst inside the steam reforming reaction portion 1 became 650°C. A power generation portion in

the fuel cell was caused to generate power in such a manner that DC power was 1.2kW. Separately from the cathode air, 20ppm toluene and 20ppm hydrogen sulfide were added to the anode air-breathing air, the selective oxidation air, and the purge air. This air was flowed through the heat exchanger 11 disposed around the CO selective oxidation portion 3 to be heated there. Then, the air was flowed through the catalytic combustor 12 disposed in contact with the shift converter 2 and including the Pt/alumina catalyst kept at 250°C. Thereafter, the air was led to the sulfur oxide absorbing portion 13 disposed in contact with the shift converter 2 and including CaO kept at 300°C. After flowing through the sulfur oxide absorbing portion 13, the air was supplied to the CO selective oxidation portion 3 at 0.5NI/min and to the anode catalyst at 0.3NI/min. This was a fuel cell power generation system A.

[0069] The fuel cell power generation system A was operated for 12h and was stopped. In a stopped state of the fuel cell power generation system A, when the temperature of the steam reforming catalyst decreased to 200°C, the air containing 20ppm toluene and 20ppm hydrogen sulfide was flowed at 10NI/ min, from the purge air supply portion 7 through the catalytic combustor 12 and the sulfur oxide absorbing portion 13, to purge the remaining gas therein and was cooled. DSS (daily Start – Stop) operation was conducted in such a manner that the fuel cell power generation system A operated for 12h and then was stopped for 12h. As a result, the fuel cell power generation system A was able to operate stably even after the operation continued for 3000h.

[0070] In the fuel power generation cell system A, the catalytic combustor 12 and the sulfur oxide absorbing portion 13 were arranged in a reversed order. The resulting fuel cell system was caused to perform the DSS operation in the same manner. As a result, stability of the fuel cell system was lower than that of the fuel cell power generation system A.

[0071] In the fuel cell power generation system A, a hydrogen sulfide absorbing portion 5 filled with MS4A pellets was provided downstream of the catalytic combustor 12, instead of the sulfur oxide absorbing portion 13 under the system A was cooled to several tens degrees C. The resulting fuel cell system was caused to perform the DSS operation. As a result, stability of the fuel cell power generation system also degraded.

[0072] From the fuel cell power generation system A, the catalytic combustor 12 and the sulfur oxide absorbing portion 13 were omitted, and in a resulting fuel cell power generation system B, air was directly flowed therethrough. As the air, air containing 20ppm toluene was used flowed for the anode air-breathing, the CO selective oxidation, and the purge. In the same manner, the fuel cell power generation system was caused to perform the DSS operation. As a result, a cell voltage increased after the fuel cell system operated for 280h, making it difficult to generate power.

[0073] Thus, since the catalyst combustor is disposed and the adsorbing agent or the absorbing agent of sulfur oxide is disposed downstream of the catalyst combustor, organic sulfur compound can be removed by catalytic combustion, and stable operation was able to be carried out even when supplied air contains hydrogen sulfide.

(Example 5)

Fig. 4 is a view schematically showing a construction of the fuel cell power generation system according to an example 4. The fuel cell power generation system of the example 4 comprises the catalytic combustor 14 having the sulfur oxide absorbing capability which is illustrated in the embodiment 2, instead of the catalytic combustor 12 and the sulfur oxide absorbing portion 13 in the fuel cell power generation system of the example 5. The construction of this fuel cell power generation system is such that PtBaO_xAl₂ZrO₃ catalyst is disposed in the catalytic combustor in the fuel cell power generation system A, and the sulfur oxide absorbing portion 13 is omitted from the fuel

cell power generation system A.

[0074] As the air for use as the anode air-breathing air, the selective oxidation air, and the purge air, the air containing 20ppm toluene and 20ppm hydrogen sulfide was used. The catalytic combustor 14 was kept at 250°C. The DSS operation was conducted in such a manner that the fuel cell system operated for 12h and then was stopped for 12h. As a result, the fuel cell system was able to operate stably even after the operation continued for 3000h.

[0075] As should be appreciated from the foregoing, by using the combustion catalysts containing the noble metal and the alkaline earth metal oxides, the fuel cell power generation system of the present invention was able to operate stably even when the supplied air contains organic compounds and sulfur compounds.

Industrial Applicability

[0076] A fuel cell power generation system of the present invention is capable of maintaining stable operation for a long time period, and is useful as a cogeneration fuel cell system for household use, or the like.

Brief Description of the Drawings

[0077] Fig. 1 is a view schematically showing a construction of a fuel cell power generation system according to an embodiment 1 of the present invention;

Fig. 2 is a view schematically showing a construction of a fuel cell power generation system according to an embodiment 2 of the present invention;

Fig. 3 is a view schematically showing a construction of a fuel cell power generation system according to an example 4 of the present invention; and

Fig. 4 is a view schematically showing a construction of a fuel cell power generation system according to an example 5 of the present invention.

Explanation of Reference Numbers

[0078] 1 steam reforming reaction portion
2 shift converter
3 CO selective oxidation portion
4 polymer electrolyte fuel cell
5 hydrogen sulfide absorbing portion
6 purge air supply portion
7 valve
8 CO selective oxidation air supply portion
9 anode air-breathing air supply portion
10 cathode air supply portion
11 heat exchanger
12 catalytic combustor
13 sulfur oxide absorbing portion
14 catalytic combustor
15 fuel supply portion
16 zeolite based adsorption and desulfurization portion
17 water supply portion
18 water evaporator
19 steam reforming reaction portion heater
20 hydrogen generator

[Name of document] Abstract

[Summary]

[Problems to be Solved] If purge air and the like contains impurities in the stopped state of the fuel cell system, a stable operation cannot be performed for a long period.

[Solving means] A fuel cell power generation system comprises a hydrogen generator 20 including a steam reforming reaction portion 1 configured to generate a hydrogen-rich gas containing carbon monoxide from a fuel containing hydrocarbon and water; a shift converter 2 configured to generate hydrogen and carbon dioxide from the carbon monoxide in the hydrogen-rich gas and the water; and a carbon monoxide removing portion 3 configured to reduce the carbon monoxide in the hydrogen-rich gas which has not been removed in said shift converter; a fuel cell 4 configured to generate power using the hydrogen-rich gas supplied from said hydrogen generator and an oxidizing gas; an air supply portion 6, 8, 9 configured to supply air to at least one of (1) a position upstream of said steam reforming reaction portion 1 in a flow of the fuel, (2) a position between the shift converter 2 and the carbon monoxide removing portion 3, and (3) a position between said carbon monoxide removing portion 3 and said fuel cell 4 in the flow of the fuel; and an impurity removing means 12, 13 configured to remove an impurity from the air.

[Selected Figure] Fig. 1

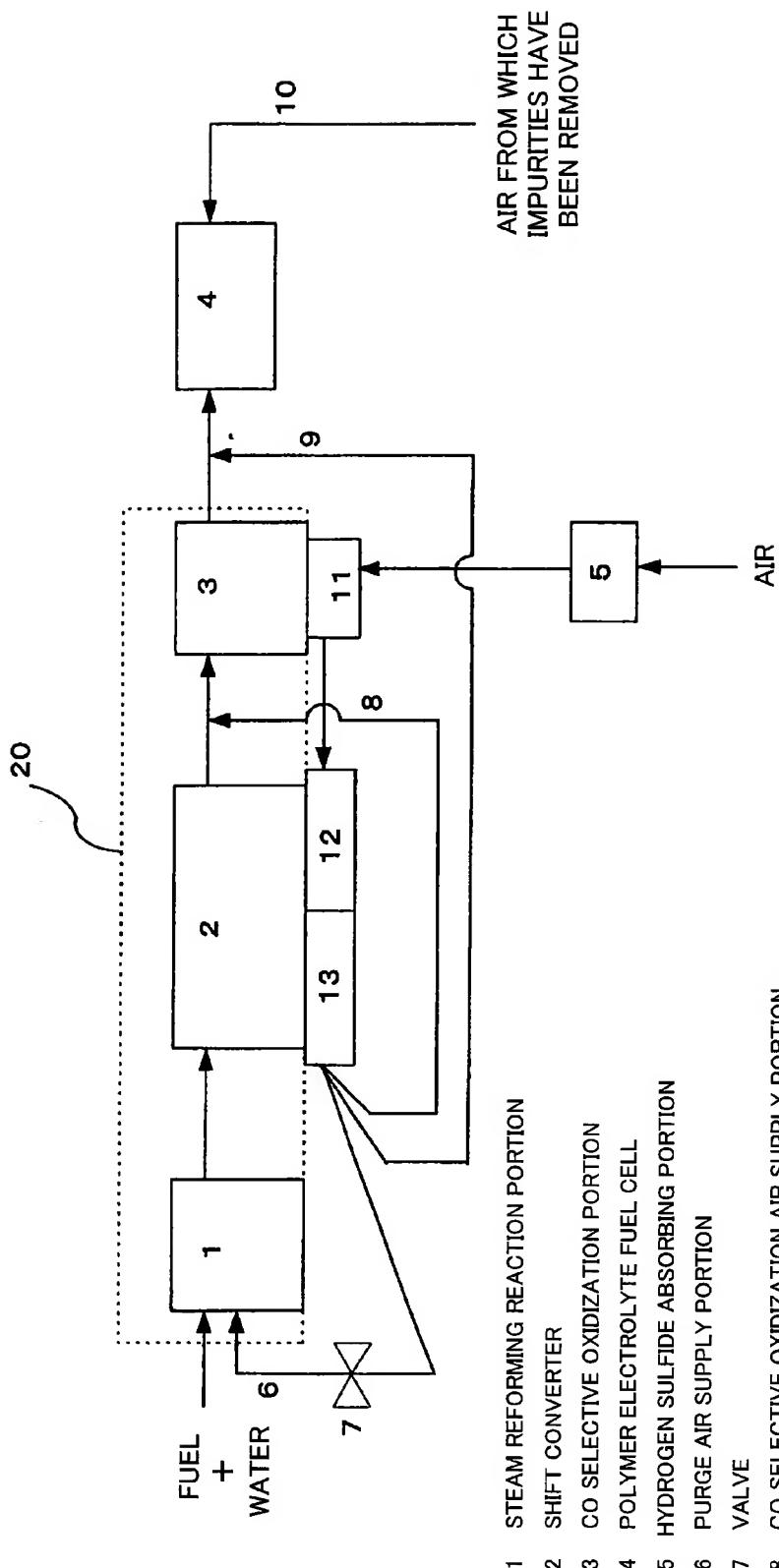


Fig. 1

Fig. 2

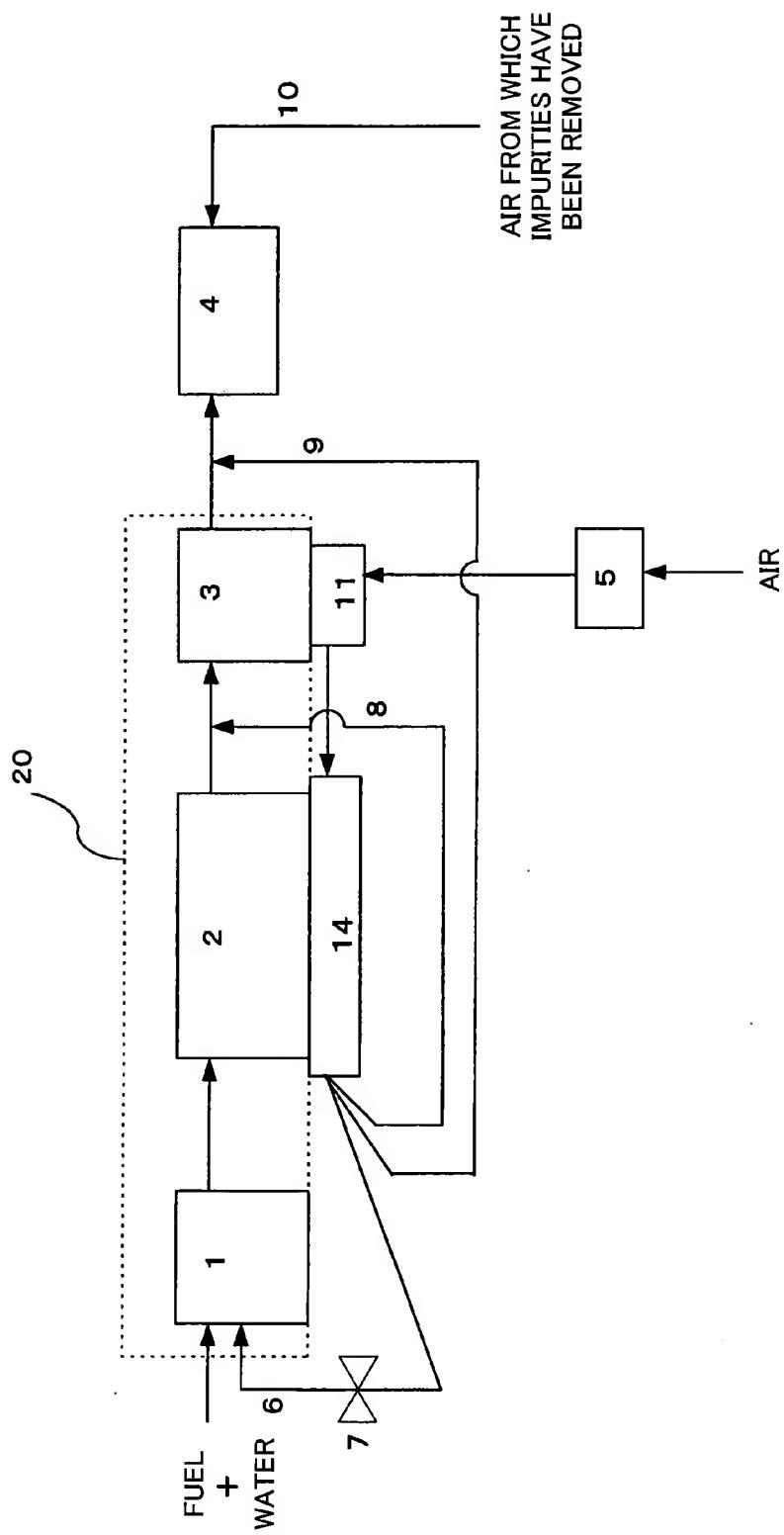


Fig. 3

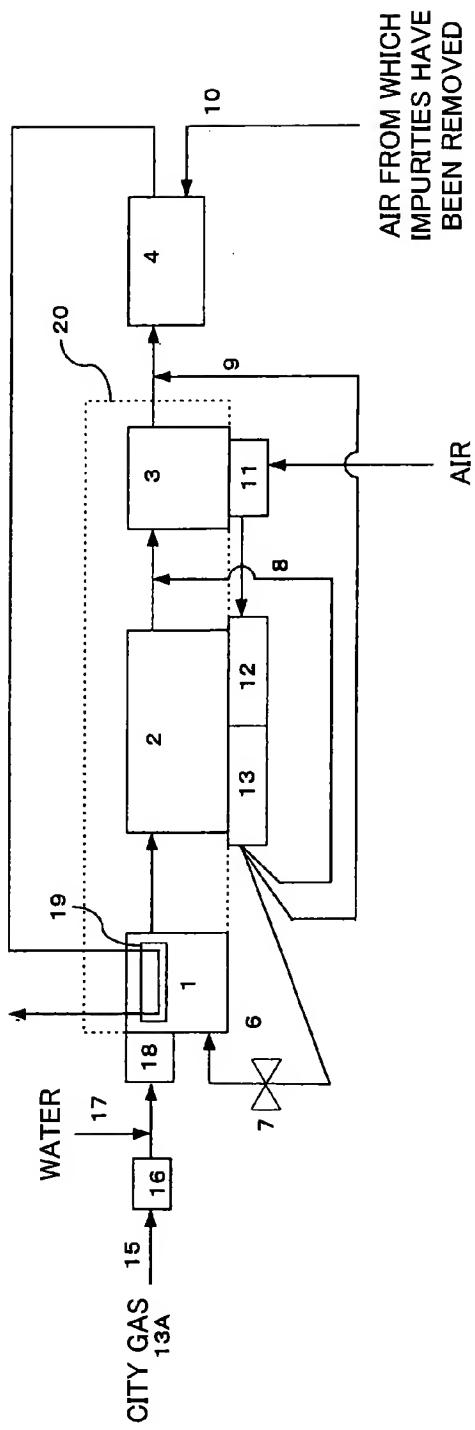


Fig. 4

